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Study of the rate of adsorption of toxic gases in shrimp ponds using Sukabumi natural zeolite

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Abstract. Shrimp production is hampered by the high level of shrimp susceptibility to death caused by pond water conditions that are not optimal. Zeolite is a very useful mining product and has properties as a molecular filter, absorber and ion exchange. Zeolite Cikembar, Sukabumi Regency is a floating rocky green tuff dominated by SiO_2. The activation process is carried out on Sukabumi zeolites by physical activation by heating. To eliminate the toxic gas NH_3, NH_4^+, and NO_2 carried out contact with the adsorption process and analyzed the UV-VIS spectrophotometry. BET SAA analysis showed zeolite surface area of 28,776 m^2 / gram. Sukabumi Zeolite at 30 grams absorbs more NH_3, NH_4^+ and NO_2 ions compared to 20 grams and 10 grams. Sukabumi's natural zeolite adsorption rate, k_{ads} (in hour-1) for NH_3 gas is 0.0724 (10 grams); 0.0896 (20 grams); 0.0922 (30 grams). Whereas NH_4^+ gas is 0.0648 (10 grams); 0.0901 (20 grams); 0.0955 (30 grams). As for NO2 gas is 0.0108 (10 grams); 0.0128 (20 grams); 0.0292 (30 grams).

Keywords: sukabumi zeolite, shrimp ponds, toxic gas, adsorption

INTRODUCTION

Development of cultivation systems from traditional to intensive with the majority shrimp ponds have potential towards increasing environmental pollution. Less optimal utilization of excessive feed will cause accumulation of organic matter. Decomposition of organic matter requires oxygen in the process, so that the availability of oxygen for the biota in it is reduced. If this happens continuously it will cause death for shrimp and other biota. Pollution materials that are difficult to decompose by microorganisms also cause hoarding and result in damage to the environment which will directly disrupt organisms that live in these environments. Organic pollution materials that function as fertilizers are actually detrimental due to algae blooms and aquatic plantscausing oxygen competition in the waters. The above factors are the cause of the decline in the body's resistance to the attack of the disease because of the poor quality of the environment, if this is left continuously then mass death will occur so that the population will decline [1].

Traditional methods for nitrogen removal from wastewater are denitrification, nitrification, chemical coagulation, adsorption, selective ion exchange, ammonia stripping, electrodialysis, filtration, and reverse osmosis [2, 3, 4, 5]. Removal processes of dissolved nitrogen compounds, can vary. For intensive RAS (Return Activated Sludge), the most common practice involves utilizing nitrifying bacteria to convert ammonia-nitrogen to nitrate-nitrogen [6]. The rate limiting step of this process is the oxidation of ammonia [7]. Incomplete nitrification occurs when a lack of NOB (Nitrite Oxidizing Bacteria) productivity is present, leading to increased concentrations of nitrite. The adsorption process is more widely used in industry because it has several advantages, which are more economical and also does not cause toxic side effects and is able to eliminate organic materials. Adsorption is a process that occurs when molecules from substances liquid or gas accumulates on a solid / liquid surface, forming a thin layer formed from

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molecules or atoms. The most important thing in the adsorption process is the selection of a good type of adsorbent [6].

The adsorption process of solutions theoretically generally lasts longer than the adsorption process on gas, steam or pure liquid [8]. This is due to the adsorption of the solution involving competition between the solution components and the adsorption site. The solution adsorption process can be estimated qualitatively from the polarity of the adsorbent and the constituent components of the solution. The tendency of polar adsorbents to more strongly absorb polar adsorbates than non-polar adsorbates, and vice versa. The solubility of the adsorbate in the solvent is the determining factor in the adsorption process, generally the hydrophilic substance is difficult to adsorb in a dilute solution. Basically, an adsorbent must have a high specific surface area, which has small diameter pores so that the adsorbate retention process by the adsorbent takes place more effectively. Specifically, the pore size also determines the adsorption of a particular compound in solution. If the adsorbent's pore size gets smaller, the adsorption capacity is greater, assuming that the adsorbed component can enter the porous cavity. The greater number of adsorbents will provide a larger surface area for the adsorbate to be desorbed. In addition, the more the amount of adsorbent will also provide greater opportunity for contact with the adsorbate molecules [9].

One of the most potential adsorbents is zeolite. Zeolite has several properties such as having dehydration properties, high cation exchange, a good catalyst, and as an agent for other compounds [10]. Increased efficiency or optimization of zeolites as adsorbents can be done through activation. The activation process aims to cleanse the pore surface, remove disturbing compounds and increase the specific surface area [11]. At the activation stage, the adsorbent is first soaked using an activating material, including HCl, HNO_3, H_2SO_4 and H_3PO_4 [12].

Figure 1. Natural Zeolite from Cikembar, Sukabumi

The chemical composition of zeolites in the Cikembar area, Sukabumi (Figure 1) is SiO_2: 68.0 - 69.8%, Al_2O_3: 11.85 - 13.16%, Fe_2O_3: 1.52 - 2.39%, CaO: 1.54-2 , 23%, MgO: 0.27 - 0.52%, Na_2O: 0.47 - 1.80%, K_2O: 2.59 - 5.0%, TiO_2: 0.03 - 0.19%, and LOI : 7.76 - 8.66%. Hypothetical resources of zeolites in Sukabumi Regency amounted to 24,151,000 tons [13].

This study aims to improve the quality of water using natural zeolite as an adsorbent so that the levels of NH_3 and NO_2 contained in water can be reduced and safe for shrimp breeding and also to aims kinetics rate of NO_2 and NH_3 adsorption using zeolite catalyst.. In this study, filters were made from PVC pipes with a pipe length of 100 cm and a diameter of 6 inches (as shown Figure 2).

EXPERIMENTAL

Zeolite Activation

Zeolite is activated using NaOH where 25 grams of zeolite are mixed with 0.5N NaOH and heated for 2 hours at 70^{o}C while stirring and then dried in an oven at 110^{o}C for 4 hours. The zeolite is then cooled in a desiccator. After drying, zeolite is ready for use. This study used 3 variations of zeolite, volume zeolite 1/3 part of pipe , volume zeolite 2/3 part of pipe and full voulme of zeolite that were filled in the pipe of filter. Experimental equipment for determining the adsorption power of sukabumi natural zeolites is shown in Figure 2.

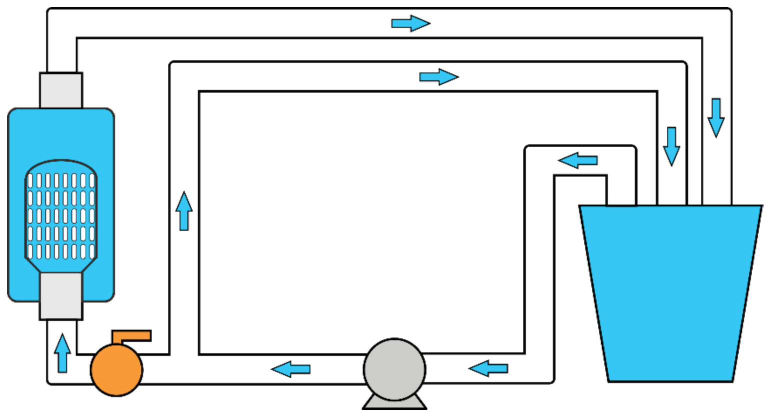

Figure 2. Experiment rig

Nitrite Levels Analysis

Analysis of nitrite levels was carried out using Diazotasi-Spectrofotometry method. In this study, samples with sulfanilic acid and N- (1-Nepthyl ethylene diamin) dihydrachloride in an acidic atmosphere (pH: 2-2.5) formed a complex compound, then placed on a spectrophotometer to be analyzed at a wavelength of 420 nm.

Ammonium Levels Analysis

Analysis of ammonium levels was carried out by the Nessler-Spectrophotometry method. In this analysis, the sample in an alkaline atmosphere is reacted with Nessler reactants to form complex compounds that are yellow to brown. The intensity of the color that occurs is measured its absorbance at a wavelength of 420 nm.

RESULT AND DISCUSSION

In this study, an initial sample of zeolite was analyzed using the BET Surface Area Analyzer Quantachrome ® ASiQwin ™ tool. The zeolite surface area analysis was carried out at UPT University Diponegoro Laboratory. From the analysis that has been done, the surface area of Sukabumi's zeolite is 28,776 m2 / gram.

Effect of Zeolite Mass on Absorbed NH_3 and NH_4^+ Levels

In this study, checking the levels of NH_3 and NH_4^+ was carried out by zeolite mass ratio in 30 grams / liter of pond water, 20 grams / liter of pond water, and 10 grams / liter of pond water. The adsorption process in the first 3 hours was carried out by sampling and analysis every 30 minutes (Figure 3 and 5). The second stage of adsorption process is carried out until it gets a constant condition. Sampling and analysis of samples is done every 1 day for 7 consecutive days (Figure 4 and 6). Samples were analyzed using a UV-VIS spectrophotometer at a wavelength of 420 nm.

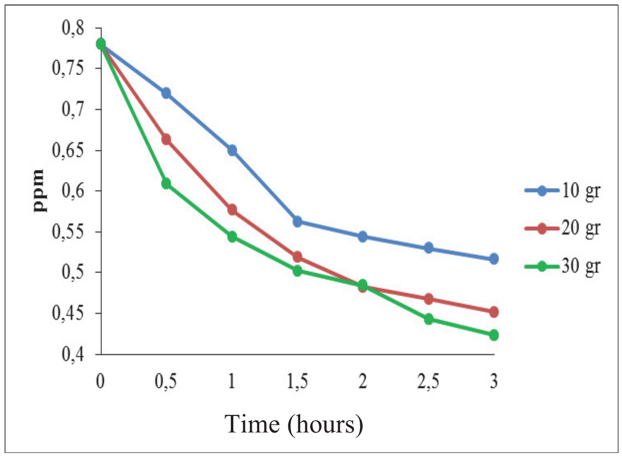

Figure 3. Effect of Sukabumi zeolite mass on NH_3 adsorption ability for 3 hours

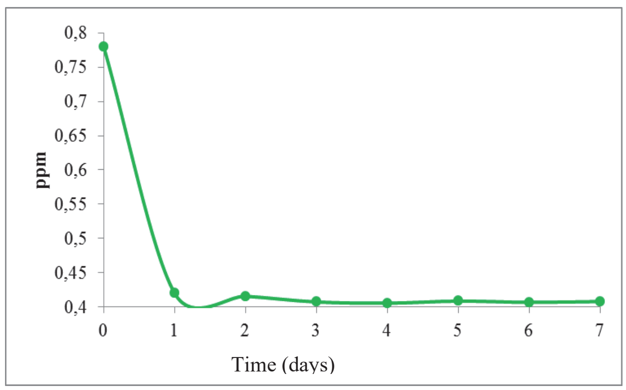

Figure 4. Effect of mass of 30 grams / l of Sukabumi zeolite on NH_3 adsorption ability for 7 days

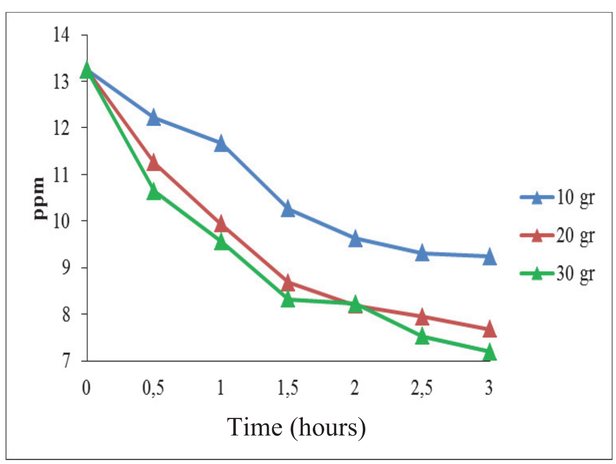

Figure 5. Effect of Sukabumi zeolite mass on NH_4^+ adsorption ability for 3 hours.

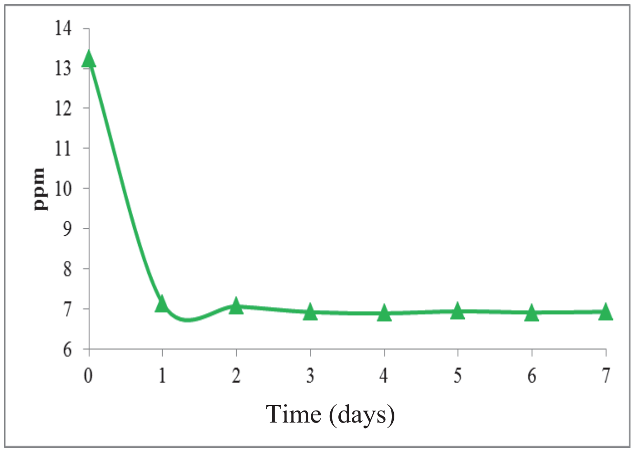

Figure 6. Effect of mass of 30 grams / l of Sukabumi zeolite on NH_4^+ adsorption ability for 7 days

Based on the results presented in Figure 3-6, it was found that zeolite at a mass of 30 grams best absorbs NH_3 and NH_4^+ levels compared to a mass of 20 grams and a mass of 10 grams.

In the first 3 hours of the adsorption process a constant trend of results has not been obtained. in zeolites 10 grams / liter, 20 grams / liter, and 30 grams / liter, the greatest decrease occurred at the same time, namely in the first 3 hours with NH_3 levels of 0.5161 ppm (10 grams); 0.4519 ppm (20 grams); and 0.4233 ppm (30 grams); and NH_4^+ content of 9,242 ppm (10 grams); 7,677 ppm (20 grams); and 7,192 ppm (30 grams). In the analysis process carried out for 7 days on zeolite 30 grams / liter, a decrease in NH_3 levels began to be constant on day 1 with the largest levels of decline occurring on day 5 with NH_3 levels of 0.408 ppm; Decrease in NH_4^+ levels began to be constant on the 1st day with the largest decreasing levels occurring on the 4th day with NH_4^+ levels of 6.889 ppm.

The large decrease in NH_3 and NH_4^+ levels is due to the more used zeolites in the adsorption process, the more contact area between the pond water sample and the zeolite surface so that the NH_3 level drops to 0.4055 ppm and NH_4^+ in the sample can drop to 6.889 ppm. NH3 gas in the sample has lower levels than NH_4^+ gas in the sample. That is because in water, ammonia comes in 2 forms, namely NH_4^+ or commonly called lonized Ammonia (IA) which is less toxic and NH_3 or Unionized Ammon (UIA) which is poisonous. The two forms of ammonia in water are in equilibrium as can be seen from the following reaction equation:

$$NH_4^+ + H_2O \leftrightarrow NH_3 + OH^-$$

The NH_3 percentage is influenced by the salinity of oxygen concentration, temperature, and water pH. The higher (alkaline) pond water pH, ammonia toxicity increases, because most are in the form of NH_3. Ammonia in molecular form (NH_3) is more toxic than in ionic form (NH_4^+). Ammonia in the form of NH_3 molecules can penetrate parts of cell membranes faster than NH_4^+ ions (Koeswojo, 2016).

Effect of Zeolite Mass on on Absorbed NO_2 Levels

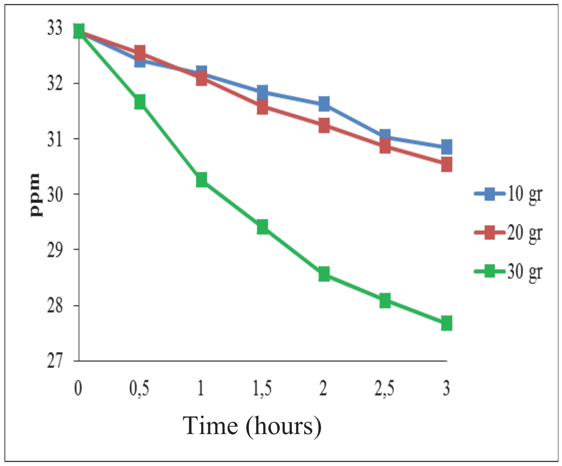

Figure 7. Effect of Sukabumi zeolite mass on NO_2 adsorption ability for 3 hours.

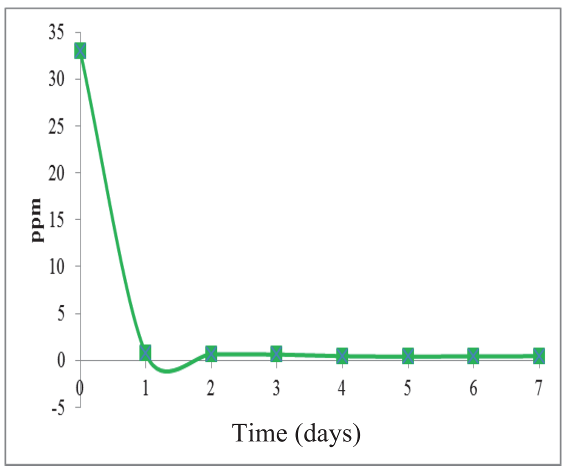

Figure 8. Effect of Sukabumi zeolite mass on NO_2 adsorption ability for 7 days.

In this study conducted to check NO_2 levels carried out with a ratio of zeolite mass to 10 grams / liter of pond water, 20 grams / liter of pond water, and 30 grams / liter of pond water. The adsorption process in the first 3 hours was carried out by sampling and analysis every 30 minutes (Figure 7). The second stage of adsorption process is carried out until it gets a constant condition. Sampling and analysis of samples is done every 1 day for 7 consecutive days (Figure 8). Samples were analyzed using a UV-VIS spectrophotometer at a wavelength of 520 nm.

From figures 7 and 8 it appears that the more zeolites used (30 grams) the more NO_2 gas is absorbed. The decrease in NO_2 gas occurs until the zeolite is used for 1 day. After that, there was no visible decrease in NO_2 gas.

Pengaruh Berat Zeolit Terhadap Konstanta Kecepatan Reaksi Zeolit.

To get the reaction rate constants, the first order reaction rate formula is used, with the following formula:

$$\ln (CAo/CA) = kt$$

where:
Cao is concentration of A at t = 0 (ppm)
CA is concentration of A at t = t (ppm)
T is time (hour)
K is adsorption rate constant ($hour^{-1}$)

From the results of the experiment graphs were made of Ln (CA / CAo) vs t. Then we get the regression equation tabulated in Table 1.

Table 1. The results of plotting the adsorption rate of NH_3, NH_4^+ dan NO_2 gases

Gas	Zeolite (gr)	Y	R^2
	10	0,0724x - 0,0399	0,9243
NH_3	20	0,0896x - 0,0146	0,9230
	30	0,0922x + 0,0169	0,9076
	10	0,0648x - 0,046	0,9465
NH_4^+	20	0,0901x - 0,0163	0,9195
	30	0,0955x - 0,0017	0,9218
	10	0,0108x - 0,0089	0,9856
NO_2	20	0,0128x - 0,0123	0,9963
	30	0,0292x - 0,0151	0,9647

Based on the data in table 1, the velocity of adsorption constant NH_3, NH_4^+ and NO_2 are obtained sequentially (in hour 1) for 10 grams is 0.0724; 0.0648 and 0.0108; for 20 grams is 0.0896; 0.0901 and 0.0128; and for 30 grams is 0.0922; 0.0955 and 0.0292. From the results obtained, the absorption rate constants for the best NH_3, NH_4^+ and NO_2 are obtained from 30 gram mass zeolites. Based on these results, the best natural zeolite absorption is found in zeolites with the largest mass (i.e 30 grams). So it can be concluded that the more natural zeolite is used (10-30 grams), the greater the reaction rate constant to be obtained and the more effective the adsorption power of the zeolite to be used.

CONCLUSION

1. Sukabumi natural zeolite which has the most content is 30 grams which absorbs more NH_3, NH_4^+ and NO_2 ions compared to 20 grams and 10 grams.
2. Sukabumi's natural zeolite adsorption rate (in hour-1) for NH_3 gas is 0.0724 (10 grams); 0.0896 (20 grams); 0.0922 (30 grams). Whereas NH_4^+ gas is 0.0648 (10 grams); 0.0901 (20 grams); 0.0955 (30 grams). As for NO_2 gas is 0.0108 (10 grams); 0.0128 (20 grams); 0.0292 (30 grams).
3. NH_3 dan NH_4^+ are more easily to adsorb with Natural zeolite from Sukabumi than NO_2 gas.

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